

INVESTIGATION OF STRUCTURAL CHANGES OF PARTICLE AGGLOMERATES WITHIN THE CHANNELS OF A WALL-FLOW FILTER UNDER THE INFLUENCE OF CONDENSED WATER

Maren Engelhardt*, Eberhard Schmidt

Institute of Particle Technology, University of Wuppertal, Wuppertal, Germany

ABSTRACT

Particle emissions from combustion engines mainly consist of soot and additives from the lubrication oil. These emissions can be almost fully eliminated by using wall-flow filters in the exhaust aftertreatment system. During regeneration, the organic soot burns away, leaving only ash in the filter channels. The overall structure of the ash agglomerates and their distribution pattern within the channel of the wall-flow filter is influenced by a multitude of different factors. These include, for example, the temperature and velocity during filter regeneration. It is suspected that another influence is water that condenses on the filter surface during a cold start event. As ash consists of partially soluble components, such as CaSO_4 , investigating the influence of condensed water on the restructuring and transportation of ash agglomerates in the filter channel will provide further insight into the deposition pattern.

A preexisting wind tunnel is modified to include a vaporizer to vary the relative humidity of the inlet air. An ash substitute can be dispersed into the wind tunnel and deposited in a wall-flow filter sample. Afterwards the filter sample can be subjected to humidifying and drying cycles. Parameters such as pressure drop, temperature, relative humidity and particle concentration can be measured. Changes in the density of the deposited particle layer alongside the filter channel wall can be determined by using an optical microscope. Additionally, structural changes of the agglomerated particles can be microscopically observed under variation of relative humidity using an Environmental Scanning Electron Microscope.

In this work, the first experimental setup will be presented. The different methodological approaches to examine the structural changes of particle agglomerates within the filter channel will be discussed.

KEYWORDS

particulate filter, wall-flow filter, ash, agglomerate structure, Environmental Scanning Electron Microscope

INTRODUCTION

Combustion engines are still commonly used in transportation and heavy-duty applications. The combustion reaction within the motor causes different emissions. One of those emissions is the particulate matter stemming from soot, wear and lubrication oil additives. The particles range in size from 7 nm to 10 μm , where especially particles smaller than 100 nm are considered to be hazardous [1], [2], [3], [4], [5]. European lawmakers therefore give limits when it comes to particulate emissions. The planned Euro-7-Norm will broaden the range of measurement for particle number emissions to include particles as small as 10 nm. Wall-flow filters (as in Figure 1) are a state of the art additive technology to almost fully reduce particle emissions. Since particle emissions partially stem from lubrication oil additives and the catalytic converter it is plausible that wall-flow Filters need to be integrated in the exhaust after treatment of gas as well as hydrogen vehicles [6], [7], [8].

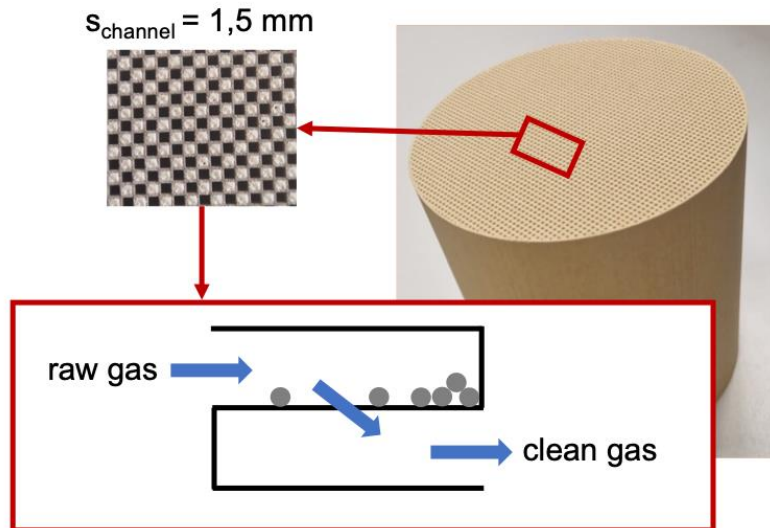


Figure 1: Wall-flow filter with schematic filter channel

Soot in the wall-flow filter is burned and converted to inert chemical compounds in the combustion process, leaving only ash in the filter channels. As ash is accumulated in the filter, it causes back pressure and leads to a negative impact on fuel consumption [9], [10]. Changes in temperature and velocity during regeneration influence the deposition pattern of ash in the wall-flow filter and have been previously researched and discussed [11], [12], [13], [14], [15], [16].

Another influence might be imposed by water that condenses on the filter during a cold start event. As the exhaust after treatment system is not yet heated up, the gaseous water from the exhaust gas will condense in the wall-flow filter, leading to a possible interaction of water droplets and already deposited ash in the filter channel. The

chemical compounds found in ash vary depending on different factors. A big influence is the chemical composition of the lubrication oil used [1], [17], [18]. Most prominent ash components are Sulfates, Metal Oxides and Phosphates from the elements Calcium, Magnesium and Zinc. The type of lubrication oil used is the main determinant of the chemical compounds in the ash and thus its behavior when the ash comes in contact with condensed water. For example, the common ash component, Calciumsulfate (CaSO_4) has hygroscopic properties and is partially soluble in water, depending on its form. These properties could lead to a change in the deposition pattern within the filter channel and influence phenomena like bridging. Therefore, condensed water could also have an impact on the back pressure.

PLANNED METHODOLOGY

Finding an ash substitute

To investigate the influence of condensed water on the agglomerated particles in the filter channels, in a first step, a suitable ash substitute material has to be found. For conducting replicable and reliable experiments, it is essential to find an ash substitute that has similar characteristics to real ash, but is less hazardous and easier to obtain. A flow chart containing suggested steps to find a suitable ash substitute is given in Figure 2.

Real ash will be chemically analyzed to determine the main components. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Energy-dispersive X-ray spectroscopy (EDX) can be used to determine the elemental components in the ash sample. This will give insight into which test materials might be compared as model ash. To analyze the adsorption capacities of the ash and possible test materials, the adsorption isotherm has to be determined by conditioning the samples in a climate chamber at different relative humidities and drying the samples in a halogen moisture analyzer. Besides the adsorption isotherm, the particle size distribution will be determined using laser scattered light. To gain a perspective on the shape and possible agglomeration microscopical analysis will be conducted. Besides using a Scanning Electron Microscope (SEM) an Environmental Scanning Electron Microscope (ESEM) can be employed to investigate ash and test material samples after being conditioned at different relative humidities. After analyzing the ash and possible test materials they will be compared and a suitable test material will be selected for the following experiments.

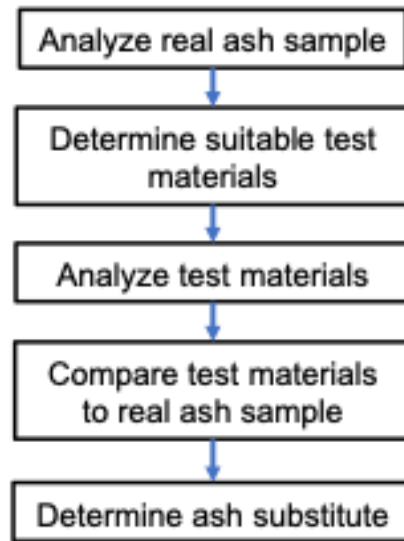


Figure 2: Proposed experimental procedure to determine a suitable ash substitute

Design of experimental setup

To investigate phenomena caused by condensed water on the stored particles in the wall-flow filter, an already existing wind tunnel is modified to include a vaporizer to vary the relative humidity of the inlet air between 40 and 80%. A filter specimen can be mounted in the wind tunnel and loaded with an ash substitute. The ash substitute will be dispersed into the wind tunnel using a brush dispersion unit. The vaporizing unit can employ a stream of humid air, with a dosing range of 0.1 to 1.25 mL/min, into the wind tunnel. With variation of the relative humidity and the duration of the humidifying process, different amounts of water mass can be applied to the filter. To protect the control and regulation unit of the wind tunnel, an adsorption dryer is added downstream the wind tunnel. New sensor inlets are to be installed right before and after the filter specimen so the relative humidity and temperature can be measured, additional to the pressure loss and particle number concentration. A schematic picture of the experimental setup is shown in Figure 3.

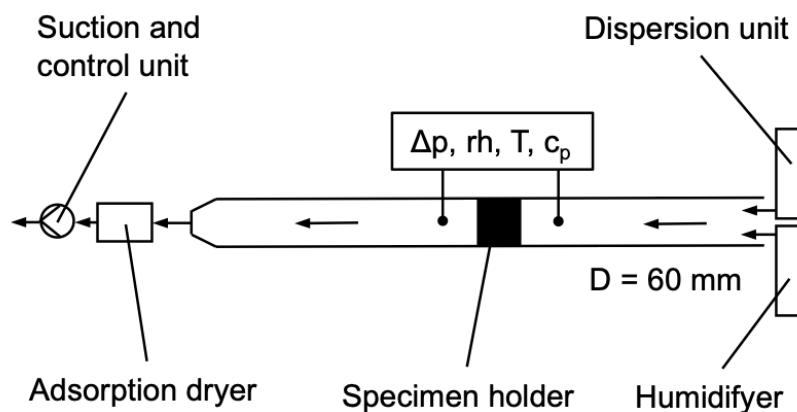


Figure 3: Schematic picture of the wind tunnel with the added modifications

The test bench will be used to load wall-flow filter samples with a defined amount of substitute ash. After a loading cycle, a filter sample can be subjected to different relative humidities, and different amounts of water mass can be applied to the filter specimen. Cooling the wall-flow filter specimen will help with the generation of condensation water. To analyze the influence of the condensed water on the filter specimen and deposited ash substitute in the filter channels the pressure drop induced by the filter will be measured. Preliminary experiments will give insight into the different parameters that can be tested to investigate the influence of condensation water on the deposited ash substitute.

The changes in the dust cake formation can be investigated using an optical microscope. Other factors such as the density of the ash substitute layer at the inlet of a channel can also be determined via optical microscopy. To see influences in the ash substitute morphology and possible changes in agglomeration after being subjected to wetting and drying microscopical analysis SEM and ESEM can be employed.

PRELIMINARY EXPERIMENTS

In first preliminary experiments, CaSO_4 Dihydrate was tested as an ash substitute. To gain insight into the particle size range, static light scattering was employed (Horiba LA950). The material was measured dry. The measurement was conducted three times. The median $x_{50.3}$ of the used CaSO_4 is $12.21 \mu\text{m}$. Twice as big compared to previously analyzed ash samples, where the median particle size $x_{50.3}$ was $6.88 \mu\text{m}$ for one ash sample and $5.57 \mu\text{m}$ for another [19]. Besides the particles simply being bigger in diameter, the test method might also need to be reevaluated, since the test material is partially agglomerated into bigger clusters of particles. Larger agglomerates can be broken apart by vibration feeder during dry measurement, but not necessarily all agglomerates can be broken down into their primary particles. Thus, a wet measurement with a suitable solvent can be additionally conducted. Further, qualitative microscopic analysis is necessary to assess the shape and size of the primary particles.

To examine the adsorption behavior of CaSO_4 , experiments in a climate chamber were conducted. To measure the adsorbed water the sample is dried in a halogen moisture analyzer (METTLER TOLEDO HX204). The moisture analyzer only measures the weight loss during the heating period and attributes that to the moisture content (MC) of the sample. The MC is given by Formula 1 and is calculated gravimetrically with the wet sample mass m_w and dry sample mass m_d :

$$\text{MC} = \frac{m_w - m_d}{m_w} \quad (1)$$

It needs to be verified that the preparation and equilibration of the samples do not

interfere with the water bound in the crystal structure of the test material, CaSO₄ Dihydrate. This is important, so the weight loss during the moisture analysis can be attributed only to adsorption of water. To test if the equilibrating and preparation of the samples did not influence the molecular crystal water, a dried sample was analyzed after 24 hours of drying at 105°C and 80°C, with a drying cycle of the moisture analyzer set to 80°C. The results of the first tests are given in Table 1.

Table 1: Moisture content of CaSO₄ samples after previous drying

Drying temperature in °C	Moisture content in %
80	0,242
105	-1,612

It can be seen that when preparing and equilibrating a sample at 105°C and then analyzing it at 80°C the sample gains weight instead of losing it due to the heating applied. This could be an indication that the preparation method prior to the moisture analysis is not well suited for the CaSO₄ Dihydrate. The weight gain after the drying process could indicate a loss of molecular crystal water during the preparation of the sample prior to the moisture analysis. Changes in the crystal water content of CaSO₄ Dihydrate can be observed starting at 65°C [20]. Thus, even the preparation with drying the sample prior to analysis at 80°C might not be suitable. To gain further insight into the mass loss due to heating, thermogravimetric analysis (TGA) should be additionally conducted for all the test dust samples and added to the proposed experimental procedure.

To obtain more insight into particle size, shape, and possible structural changes of particle agglomerates under the influence of condensed water, first tests with ESEM were conducted. A room temperature, not previously dried, sample of CaSO₄ Dihydrate was prepared and investigated under ESEM. To simulate condensation the sample was then artificially wetted before further pictures from the same sample area were taken again. The images can be seen in Figure 4. It can be seen that the structure of the particles changed. Whereas the particles previously to wetting were angular with distinct edges (Figure 4a). Wetting led to a change in the crystal structure of the particles. The CaSO₄ crystals are acicular (Figure 4b), like they would be in water.

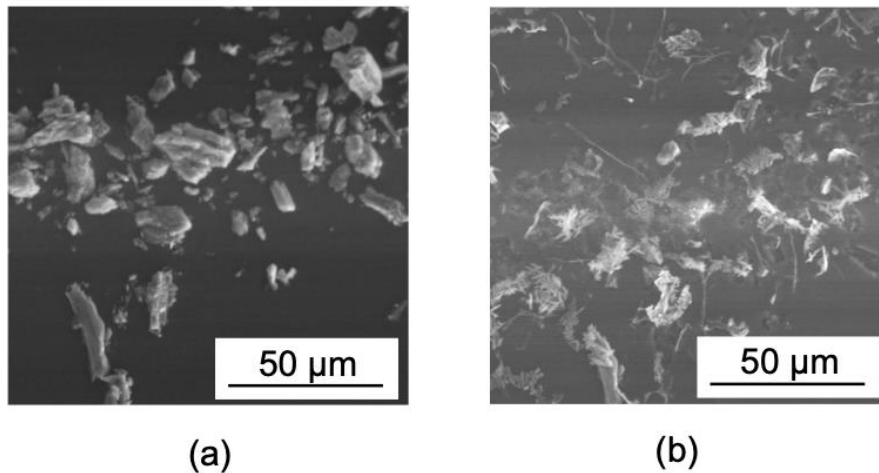


Figure 4: Sample of CaSO_4 dry (a) and after wetting (b)

Investigating the influence of condensed water on the crystal structure of the suitable test materials for ash substitutes and the ash itself seems to be a vital step in describing possible restructuring processes caused by condensed water inside a wall-flow filter.

CONCLUSION AND OUTLOOK

Understanding the interactions of condensed water and ash particles trapped in a wall-flow filter is a vital step to better describe its long-term behavior. To investigate the influence of condensed water on ash particles a test protocol is proposed where a substitute ash is to be found by analyzing different chemical components present in an ash sample. This ash substitute can then further be used to conduct model experiments in a modified wind tunnel to observe changes in back pressure due to condensed water. First preliminary experiments helped in adjusting the experimental protocol for determining a suitable substitute material to model properties of real lubricant derived ash. The first test results highlighted the need to further investigate changes in crystal structure of the particle when in contact with water and possible changes in crystal water bound within the particles.

In future studies the presented method will be applied to real ash samples and possible substitute materials to gain insight into changes of the particles, their agglomerates as well as structural changes in the deposition pattern inside the channels of a wall-flow filter.

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